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cont. the lignocellulosic material consists essentially of esterifying the hydroxyl groups of the lignin of the lignocellulosic material.—

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#### REMARKS

Reconsideration of the above-identified patent application, as amended, is respectfully requested. The claims have previously been rejected in prior applications as unpatentable over the prior art, primarily the Teng patent 3,788,984. Applicants submit that the claims patentably distinguish over the prior art as set forth hereafter. In addition, claims 8 and 9 were previously objected to as being dependent on cancelled claim 7, and this ground for objection has been removed by the amendment of those claims to depend from claim 1.

The Teng patent has been cited as showing the esterification of lignocellulosic materials with acetic anhydride in a process which appears to be identical with that of the present invention. However, there is a substantial distinction between the process of Teng and that of the present invention, the consequence of which is that Teng does not anticipate or make obvious the present process and resulting products.

The Teng patent does not involve the esterification of lignocellulosic material, but rather applies a severe process which is distinguishable from the claimed one. Teng employs perchloric acid in his process. Specifically, the process of Teng for producing, for example, cellulose acetate involves treatment of the cellulose source material with acetic anhydride in the presence of perchloric acid for 2-5 minutes at 0-5°C (column 4, lines 21-27). Perchloric acid is an aggressive reagent which is required to "smash-up"

cellulose to make it reactive. If the cellulose source material being treated includes lignin and hemicellulose, then the latter materials can be expected to be washed out of the material due to the aggressive and acidic processes used by Teng.

This result is not surprising given the premise of Teng that the cellulose, rather than any lignin, is to be esterified. This focus of Teng is clear from the patent, and is readily demonstrated by the fact that the preferred cellulose source material for Teng is cottonseed hulls, which do not contain lignin. Indeed, Teng indicates that any lignin or hemicellulose which may be present are deemed to be impurities.

~~Enclosed~~ is a copy of the reference Methods in Carbohydrate Chemistry, cited by Teng. The method involving perchloric acid as used by Teng relates to the production of cellulose acetate, but makes no reference to esterification of lignin (see pages 196-197).

By contrast, the present invention specifically relates to the esterification of the hydroxyl groups of the lignin. The method involves absorption of the esterifying agent (e.g., acetic anhydride) by the lignocellulose material, which is then heated. No perchloric acid or other aggressive catalyst is used, and little, if any, substitution of the cellulose occurs because it has a crystalline structure with relatively inaccessible reactive groups. Thus, at one level there is the present process which treats lignocellulosic material to esterify the hydroxyl groups of the lignin with little if any impact on the cellulosic material. At a totally different level is the Teng process which employs much more severe conditions – involving an aggressive agent – which will drive out any lignocellulosic material with esterifying the hydroxyl groups of the cellulosic material.

With this background, it is apparent that the Teng patent is in distinct contrast to the present invention. In fact, the Teng patent may be considered to teach AWAY from the present invention. It considers the lignocellulosic materials to be impurities to be cast out of the final product. The present invention encompasses the discovery that the previously considered to be deleterious – are in fact useful if properly treated.

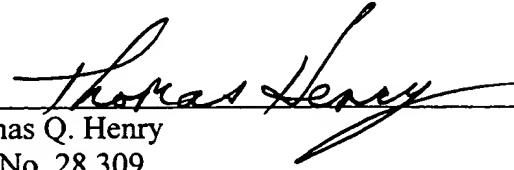
The contrast of the Teng patent and present invention is further highlighted by a comparison of the resulting products. The Teng patent indicates that the cellulose acetates are able to absorb up to 15 times their weight of crude oil ) (column 2, lines 46-49). Materials prepared and used in accordance with the present invention, can absorb up to 28 times their weight of crude oil.

The claims remaining in the application are distinguishable over the prior art on the foregoing bases. New claim 25 provides a further distinction in requiring that the esterification of the hydroxyl groups of the lignocellulosic material consists essentially of esterifying the hydroxyl groups of the lignin of the lignocellulosic material. This further emphasizes the unobvious difference over the Teng patent, which could not be essentially directed to esterifying the hydroxyl groups of the lignocellulose for reasons already indicated. In view of these grounds of distinction, and for reasons previously argued, it is submitted that the Fahlvik reference cannot be combined with the Teng patent in a manner to suggest or make obvious the present invention.

Reconsideration of the above-identified patent application, as amended, is

therefore respectfully requested and allowance of the claims in the application is solicited.

Respectfully submitted,

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METHODS IN CARBOHYDRATE CHEMISTRY VOL III  
R. L. WHISTLER, ED. ACADEMIC PRESS 1963

## CELLULOSE ACETATE

### [30] Acetylation of Cellulose

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#### Introduction

A cellulose acetate is characterized mainly by its degree of substitution (average number of acetyl groups per anhydro-D-glucose unit), its degree of polymerization (average number of anhydro-D-glucose units per molecule), and by the distribution of unesterified hydroxyl groups among the primary (6-position) and secondary (2- and 3-) positions.

Methods are given for preparing and characterizing a variety of cellulose acetates. The preparative methods are designed to use simple laboratory equipment and to apply to a variety of celluloses. Alternative analytical methods are given in following sections, so the use of specialized equipment can be avoided if necessary. Equations are presented for calculation of degree of substitution (D.S.) and an approximate value for the degree of polymerization (D.P.) from analytical data.

Cellulose acetate is ordinarily prepared by reaction of cotton linters or wood pulp with acetic anhydride using glacial acetic acid as a solvent and sulfuric acid as a catalyst. The triacetate is not formed, but rather a cellulose acetate sulfate triester. This may be isolated as such, or the combined sulfate may be removed, without loss of acetyl, giving a high-acetyl cellulose acetate. The amount of combined sulfate in the triester, and in turn the hydroxyl content of the resulting high-acetyl cellulose acetate, depends on the amount of sulfuric acid used.

If a true cellulose triacetate is desired, it can be made by a fibrous process or by re-esterifying a commercial acetone-soluble cellulose acetate in solution, in both cases using a non-combining catalyst, such as perchloric acid.

Cellulose acetate of low primary hydroxyl content is prepared by a selective partial reacetylation of a far-hydrolyzed cellulose acetate.

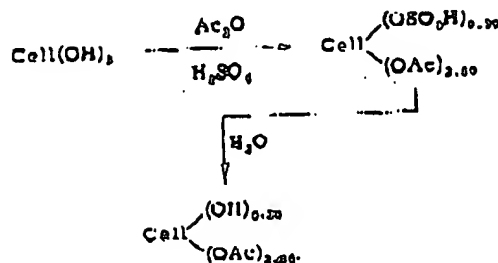
For regeneration of cellulose from cellulose acetate see Vol. III [17].

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## CELLULOSE ESTERS

## Procedure

## High-acetyl Cellulose Acetate



Ten g. of acetylation-grade cotton linters is immersed in distilled water and, after 15 min., is pressed out on a Büchner funnel using a thin sheet of rubber. The wet cake is transferred to a pint, screw-capped bottle and covered with 150 ml. of glacial acetic acid. After being shaken occasionally during 15 min., the cellulose is pressed out as before. The cellulose is given a second dewatering in the same manner. The resulting aqueous acid is saved for diluting the solution before precipitation. If the acetic acid from this dewatering has a melting point below 13°, a third dewatering is done; however, two dewaterings usually suffice.

The cellulose, with about 20 g. of adhering acetic acid, is placed in a pint screw-cap bottle containing 180 ml. of acetic acid and 1.0 ml. of conc. sulfuric acid at 25°. The mixture is shaken vigorously for 1 min., and 50 ml. of acetic anhydride is added. The mixture is again shaken vigorously for about 1 min. The fibers soon become very mushy, and further mixing is accomplished by occasionally inverting the bottle. There is a temperature rise of about 10° within 5 min. after adding the anhydride. After 15-30 min., there results a viscous solution which contains air bubbles but is practically free from fiber and grain. If isolated clumps of fibers persist at this point, the mixture should be stirred at high speed for a few seconds with a Lightning Mixer or similar equipment.

After 30-60 min., when the solution is free from fiber and grain, a mixture of 7.5 ml. of water and 17.5 ml. of acetic acid is added with high-speed stirring. This destroys the excess anhydride, giving a temperature rise of about 25°. It also provides 0.5-1.0% of water in the acetic acid, which is very effective for removal of combined sulfate without loss of acetyl (1). After 30 min., the solution is diluted as needed with the aqueous acetic acid recovered from the dewatering process. The product is precipitated in distilled water, washed, stabilized with sodium carbonate, and dried as de-

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described in the following section. It contains 43.0-43.2% of acetyl (60.0-60.8% of combined acetic acid), corresponding to 2.70-2.82 acetyl groups per anhydro-D-glucose unit. The hydroxyl content is 1.1-1.3% of which 75-80% is in the primary position. The product is soluble in dichloromethane (methylene chloride)-methanol (90:10 w/w) but not in acetone.

*Precipitation and Washing Details*

A 4-quart stainless steel or enamelled beaker is about two-thirds filled with distilled water, and a high-speed stirrer is placed slightly off center. The water is brought into vigorous turbulence, and the solution of the ester is poured in slowly. The condition of the precipitate is checked after a small amount of the ester has been precipitated. If there are clumps of gelatinous material, the stirring should be increased or the cellulose ester solution should be diluted further. If the precipitation liquid has a milky appearance, the speed of stirring should be decreased. The rate of pouring may be increased as the concentration of acetic acid builds up in the precipitation bath.

The cellulose ester is pressed out on a Büchner funnel or, more conveniently, squeezed out by hand in a lint-free cloth bag. The ester is returned to the beaker with distilled water and stirred slowly for a few minutes. The process is repeated 3 or 4 times until one drop of 0.6N sodium hydroxide is sufficient to impart a pink color to phenolphthalein in 100 ml. of the wash liquid.

The ester is then stirred in distilled water, and phenolphthalein is added to the suspension. Solid sodium carbonate is added, a few grains at a time, just sufficient to impart a permanent pink color to the indicator. This neutralizes any remaining acetic acid and forms a sodium salt with the trace of combined sulfate in the cellulose ester. After stirring for a few minutes, the ester is pressed out and given a final wash with distilled water to remove any excess of stabilizing salt. Finally, the ester is dried at room temperature or in an oven in a current of air at about 60°.

*Starting Materials*

This method gives good results on cotton linters, surgical absorbent cotton, acetylation-grade wood pulp, and Whatman No. 4 filter paper. The latter two materials require sufficient stirring with water to break up their sheet form before acetylation.

*Activation*

Efficient activation is necessary to obtain rapid acetylation and good clarity (2). Some samples of cellulose may be acetylated satisfactorily by the above method without the activation with water and dewatering.

TABLE I  
Variations in Method of Preparation and Viscosity of Product

Example	Interval between additions of catalyst and anhydride, 25°	Interval between clearing of solution and addition of water, 25°	Intrinsic viscosity in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (90:10 w/w)	$\eta_{sp}/C$
A	1 min.	None	1.97	1.27
B	1 hr.	None	1.43	1.20
C	1 min.	10 hr.	1.13	0.95

In this case the air-dry (not dried at 110°) cellulose is added directly to acetic acid and allowed to stand overnight or longer before adding catalyst and anhydride. The results, however, may be extremely variable depending on the previous history of drying and storage.

#### Viscosity

The method gives a product (Example A in Table I) with an intrinsic viscosity of approximately 2.0 in dichloromethane (methylene chloride)-methanol (90:10 w/w), corresponding to a degree of polymerization of about 340. When products of lower viscosity are desired, they can be obtained by degrading the cellulose before acetylation (Example B) or the cellulose acetate after acetylation (Example C).

#### Cellulose Acetate Sulfate Sodium Salt

In the above procedure, at the point where a clear solution is first formed, the major portion of the sulfuric acid is combined with the cellulose.

The product may be isolated by neutralizing the catalyst, without addition of water, using an excess of base; such as an acetic acid solution of pyridine or sodium acetate. After diluting as needed with acetic acid and precipitating as described above, the product is obtained in a gelatinous, almost transparent form. It is readily washed, however, using large amounts of water and is converted to the sodium salt when stabilized as described above.

The amount of combined sulfate in the product depends on the amount of catalyst used but decreases when neutralization of the catalyst is delayed after the esterification solution has clarified (3).

#### Cellulose Triacetate, Fibrous Process



Ten g. of acetylation-grade cotton linters is activated and dewatered as described above.

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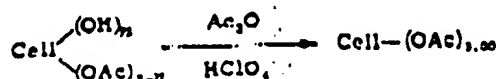
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ing a mixture of 80 ml. of acetic acid, 100 ml. of toluene, and 0.5 ml. of 72% perchloric acid, previously adjusted to 25°. The mixture is shaken vigorously for 1 min. Then 50 ml. of acetic anhydride is added, and the mixture is again shaken vigorously for about 1 min. The mixture is stirred with a Lightnin Mixer or similar equipment throughout the remainder of the reaction.

After about 15 min., a small sample is removed, pressed dry on paper towels, and tested for solubility in dichloromethane (methylene chloride)-methanol. Further tests are made, if necessary, until solubility is found to be complete. This is usually achieved after a reaction time of 20-60 min. The cellulose triacetate is pressed out on a Büchner funnel or in a cloth bag, washed once with ethanol, and then with water as described in the preceding section for precipitated samples.

The product is soluble in dichloromethane (methylene chloride)-methanol (90:10 w/w), insoluble in acetone, and has less than 0.05% of hydroxyl groups by the carbanilation method (Vol. III [38]).

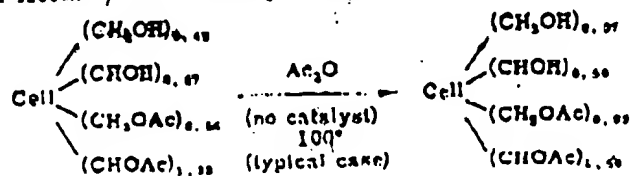
## Cellulose Triacetate, Solution Process



Twenty-five g. of acetone-soluble cellulose acetate, dried 2 hr. at 110°, is dissolved in a mixture of 450 ml. of acetic acid and 50 ml. of acetic anhydride. This is conveniently accomplished by tumbling overnight in a quart, screw-capped bottle. A solution of 1.0 ml. of 72% perchloric acid in 10 ml. of acetic acid is added with high speed stirring. There is a sharp rise in temperature, and acetylation is essentially complete after 1-2 min. After 30 min., the product is precipitated, washed, and stabilized as described above. The product is soluble in dichloromethane (methylene chloride)-methanol (90:10 w/w) and contains no detectable hydroxyl (<0.06%) by the carbanilation method (Vol. III [33]).

This reacetylation is adaptable to a wide range of cellulose acetates with little loss in degree of polymerization. However, native cellulose, even after activation, yields a grainy reaction solution unless the reaction time and/or temperature is increased considerably.

## Cellulose Acetate, Low Primary Hydroxyl



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The starting material is a far-hydrolyzed cellulose acetate containing 30-35% of acetyl. It may be prepared from the cellulose acetate as described in Vol. III [31] by hydrolysis in 90-95% acetic acid for 5 days or more. The lower the acetyl content and the percentage of primary hydroxyl groups of the starting material, the lower will be the percentage of primary hydroxyl groups in the partially reacylated product.

One hundred g. of cellulose acetate (33.4% of acetyl; 40% of the hydroxyl in the primary position), dried 2 hr. at 110°, is dissolved in 1 liter of acetic acid contained in a 2-liter flask which is heated on a steam bath and is fitted with a stirrer. One hundred ml. of acetic anhydride is added, and the heating and stirring are continued for 7 hr., after which the product is isolated in the usual manner. The product contains 39.5% of acetyl groups, and only 12% of its hydroxyl groups are in the primary position.

Catalyzed acetylations are slightly less selective for the preferential acetylation of primary hydroxyl groups; the uncatalyzed acetylation at room temperature is even more selective than at steam bath temperature, but requires several weeks to accomplish (4).

#### References

- (1) C. J. Malm and L. J. Tanghe, *Ind. Eng. Chem.*, **47**, 906 (1955).
- (2) C. J. Malm, K. T. Parker, D. C. May, and R. D. Lefferts, *Ind. Eng. Chem.*, **44**, 2004 (1952).
- (3) C. J. Malm, L. J. Tanghe, and D. C. Laird, *Ind. Eng. Chem.*, **38**, 77 (1946).
- (4) C. J. Malm, L. J. Tanghe, D. C. Laird, and O. D. Smith, *J. Am. Chem. Soc.*, **75**, 80 (1953).

### [31] Hydrolysis of Cellulose Acetate

BY LEO J. TANGHE, LEO H. GERNING AND J. WARREN MENCHI

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#### Introduction

Partial hydrolysis of cellulose triacetate or high-acetyl cellulose acetate considerably modifies its properties. This hydrolysis is ordinarily accomplished, without isolating the fully esterified ester, by adding water beyond that required by the excess acetic anhydride and by holding the solution until the desired acetyl content is reached. Of particular interest is the range of acetone solubility which extends from approximately 35 to 42% of acetyl. (Products isolated in this range of acetyl content during the course of acetylation are not homogeneous and are not soluble in acetone.)

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